

C. MODELS THAT CAN EXPLAIN THE SORPTION DATA

Radionuclides are known to be adsorbed by mineral surfaces in rocks and soils. The strongest interactions between aqueous species and mineral surfaces are the formation of electrostatic and covalent bonds. Ion-exchange reactions are primarily electrostatic interactions (outer electronic sphere and diffuse layer). Inner-sphere surface complexes form a chemical bond (to the mineral surface) that is more covalent. The electrostatic interaction does not have the same degree of selectivity between aqueous ions of like charge as does the more covalent inner-sphere surface complex. Stable inner-sphere complexes can be formed even when the mineral surface charge is the same as the aqueous ion. On the other hand, the adsorption of metal ions via cation exchange will only occur on surfaces of opposite charge and is affected by such common components of groundwater as sodium. Both of these processes can, in principle, be modeled using a triple-layer surface-complexation model. There are significant differences between the cation exchange in zeolites and clays and the formation of outer-sphere complexes on metal oxides. For this reason, cation exchange and surface complexation will be treated separately.

Cation Exchange

Description of the process

The cation-exchange capacity of aluminosilicates is often high. Zeolites, such as clinoptilolite and mordenite, and clays, such as montmorillonite, have enormous surface areas because of their channeled and layered structures, respectively. The surfaces are negatively charged because they are composed of tetrahedrally bound silica and alumina. Aluminum requires an additional electron in order to share electrons equally between four oxygen atoms in a tetrahedral structure. The excess negative charge is balanced by an alkali-metal or alkaline-earth cation. These cations can be exchanged for cationic radionuclides. The extent to which a radionuclide is adsorbed depends on the selectivity

for that cation. The equilibrium reaction can be represented, for example, as follows:



where AlO^- represents a tetrahedrally bound aluminum site. The equilibrium expression for this reaction is

$$K = \frac{[\text{AlO}^-\text{Cs}^+][\text{Na}^+]}{[\text{AlO}^-\text{Na}^+][\text{Cs}^+]}, \quad (17)$$

where K is the selectivity coefficient. For a mineral with one type of cation exchange and a binary aqueous salt, this expression can be rewritten in terms of the solid-phase concentration, q , of one of the cations of interest (here, cesium). The result is

$$q = \frac{KQc}{(K-1)c} + c_o, \quad (18)$$

where, in this case, $q = [\text{AlO}^-\text{Cs}^+]$, c is the solution-phase concentration of the cation, $[\text{Cs}^+]$, c_o is the total solution-phase cation concentration ($[\text{Cs}^+] + [\text{Na}^+]$), and Q is the cation-exchange capacity of the solid phase ($[\text{AlO}^-\text{Cs}^+] + [\text{AlO}^-\text{Na}^+]$). Equation 18 is nearly identical to the Langmuir isotherm (derived for the adsorption of gases on solids) and will be referred to as such in the remainder of this report.

Factors affecting cation exchange

There are many factors affecting cation exchange in natural systems, such as competition between multiple cation-exchange sites, selectivity between cations in groundwater and the radionuclide of interest, and aqueous speciation of the radionuclide, to name a few. Competition between multiple cation-exchange sites leads to nonlinear adsorption isotherms. The selectivity between cations depends on the geometry of the cation-exchange site and the relative degree of hydration of the aqueous cations. In clays and zeolites, the selectivity coefficient increases from more- to less-hydrated cations, so that the order for alkali metal cations is lithium < sodium < potassium < rubidium < cesium (see McBride 1994, for example). Aqueous speciation can change the charge and the net size of the ions. In addition, there are sites in

minerals, such as analcime, that can exclude larger ions, like cesium, entirely.

In principle, an equilibrium code, such as EQ3/EQ6 (Wolery 1983), could predict cation exchange if selectivity coefficients for all the significant cationic constituents of groundwater were known for each cation-exchange site in each mineral contained in tuff. In practice, few selectivity coefficients are known for single minerals, let alone individual exchange sites.

Experimental methods

The most useful experiment for determining sorption thermodynamic data is the adsorption isotherm. The adsorption isotherm is a measurement of the solid-phase concentration versus the aqueous-phase concentration at constant temperature. If the behavior of the isotherm is ideal, it can be described by a Langmuir isotherm (Eqn. 18), which can be the case only if there is one type of cation-exchange site and if outer-sphere surface complexation is not significant.

Pure cation exchange cannot be measured in a system also capable of surface complexation, whether that system is a whole rock or a clay mineral. By varying the pH and electrolyte concentration, either surface complexation or cation exchange can be enhanced, which allows information about both mechanisms to be extracted from the data. The Swiss nuclear waste program has made great progress in developing such methods (Baeyens and Bradbury 1995a, 1995b; Bradbury and Baeyens 1995).

Ion-exchange models

One approach that allows the determination of the free energy of exchange in even nonideal systems is that of Gaines and Thomas (1953). This approach requires that the adsorption isotherm be taken from one end member (for example, sodium saturated) to the other end member. In this case, the free energy of exchange, ΔG° , is related to the definite integral over the mole ratio of cations from one end member to the other as follows:

$$\Delta G^\circ = -\frac{RT}{Z_1 Z_2} \left[(Z_2 - Z_1) + \int_0^1 \ln K \, dA \right], \quad (19)$$

where Z_1 and Z_2 are the charges on the original and incoming cations, respectively, A is the mole ratio of the incoming cation, R is the gas constant, and T is absolute temperature. This approach cannot, in general, be used to calculate distribution coefficients because it cannot describe nonideal solid solutions.

Ion exchange arises from two distinctly different chemical structures on the surfaces of minerals. One is the incorporation of aluminum (with a valence of 3) in a tetrahedrally bonded silicate structure. The other is the amphoteric reaction of metal oxides with acids and bases. The former is a negatively charged surface of a fixed nature with the charge compensated by cations. The latter can be either negatively or positively charged depending on the pH of the aqueous phase. The exchange capacity of the former structure is fixed, whereas the exchange capacity of the latter depends on pH, ionic strength, and the concentration of specific inner-sphere complexing ligands. The adsorption of exchangeable ions on an activated metal-oxide surface is a form of outer-sphere surface complexation.

The selectivity in aluminosilicates for a given radionuclide over another has been shown to be not a simple binary-exchange process, even when the solution is a simple binary aqueous solution, because not all positions in aluminosilicate are equivalent with respect to crystallographic structure. For example, there can be differences due to steric crowding. These differences have been studied by deconvolving the ion-exchange isotherm.

The method of deconvolution has been shown to be effective in studying structural effects on ion selectivities in synthetic zeolites (Triay and Rundberg 1989a). In that study, the shape of the ion-exchange isotherm was shown to be due to differences in the crystallographic structure at the ion-exchange sites. This interpretation could not be made on the basis of the deconvolution of adsorp-

tion isotherms without spectroscopic data. However, the method of deconvolution does allow a quantitative correlation of the ion-exchange data with the spectroscopic data.

The method of analysis assumes ion exchange. The thermodynamics of ion exchange have been reviewed by Cremers (1977). The selectivity coefficient K for the hypothetical ion-exchange process in the reaction



is given by

$$K = \frac{q_2 a_1}{q_1 a_2} , \quad (21)$$

where a_1 and a_2 are the activities in solution of the cation to be exchanged and the entering cation, respectively, and q_1 and q_2 are the corresponding concentrations of these cations in the solid phase expressed as moles of cation per gram of the exchanger.

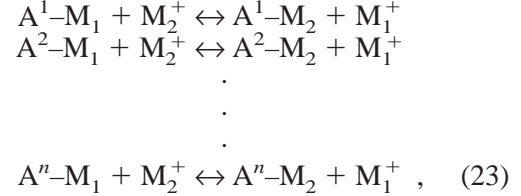
As a result of mass-balance considerations, Eqn. 21 can be rewritten as

$$q_2 = \frac{KQ\gamma_2 C_2}{C_o\gamma_1 + (K\gamma_2 - \gamma_1)C_2} , \quad (22)$$

where Q is the total moles of exchangeable sites per gram of exchanger ($Q = q_1 + q_2$), C_2 is the concentration of the entering cation in the liquid phase, C_o is the total concentration of cations in the liquid phase ($C_1 + C_2$), and γ_1 and γ_2 are the activity coefficients in the solution phase of the cation to be exchanged and the entering cation, respectively (that is, $a_1 = \gamma_1 C_1$ and $a_2 = \gamma_2 C_2$).

Equation 22 represents the dependence of the solid-phase concentration on the liquid-phase concentration. It has the mathematical form of the Langmuir isotherm. In general, adsorption isotherms do not follow the Langmuir isotherm. Many authors have successfully described cation exchange in terms of multiple sites (Barrer and Klinowski 1972; Barrer and Munday 1971; Brouwer et al. 1983). The underlying assumption

of the deconvolution method is that the nonideality of the adsorption isotherm is due to adsorption at multiple sites. Consequently, one may consider a set of simultaneous equilibria



where $\text{A}^1, \text{A}^2, \dots, \text{A}^n$ represent different sites in the ion exchanger.

The solid-phase concentration of the cation M_2^+ in site i is given by

$$q_2^i = \frac{K^i Q^i \gamma_2 C_2}{C_o \gamma_1 + (K^i \gamma_2 - \gamma_1) C_2} , \quad (24)$$

and the total solid-phase concentration of M_2^+ is given by the sum

$$q_2 = \sum_n q_2^i = \sum_n \frac{K^i Q^i \gamma_2 C_2}{C_o \gamma_1 + (K^i \gamma_2 - \gamma_1) C_2} . \quad (25)$$

This approach is further generalized by replacing the sum in Eqn. 25 with the integral equation

$$q_2(C_2) = \int q_2(C_2, K) f(K) dK , \quad (26)$$

where $f(K)$ is a distribution function for the selectivity coefficient of the exchange.

The idea of expressing the heterogeneity of the exchanger in terms of a distribution function has been previously presented (Brouwer et al. 1983; Adamson 1982; Sposito 1979, 1980, 1984; Kinniburgh et al. 1983). Equation 26 is a Fredholm integral of the First Kind, and the methodology used here to solve for $f(K)$ has been described by the authors (Triay and Rundberg 1987, 1989b) and others (Butler et al. 1981; Britten et al. 1983). The computer code INVPOS has been written (Travis 1996) to solve Eqn. 26. INVPOS uses the method of Butler, Reeds, and Dawson (1981) to find an optimal solution using regularization with a positivity constraint.

Semiempirical adsorption isotherms, such as the

Freundlich isotherm, are derived by evaluating the integral (Eqn. 26) using closed-form approximations and assuming some arbitrary site energy distribution. These approaches are only valid for data interpolation because they do not provide insight into the actual mechanism of adsorption.

Description of cation-exchange sites in Yucca Mountain tuff

Detailed adsorption isotherms adequate for the analysis described above have not been done for the Yucca Mountain Project. Measurements of the mineralogy of Yucca Mountain tuff have shown an abundance of minerals known to have both pH-independent cation-exchange sites (that is, tetrahedral aluminum sites) and surface-complexation sites (for example, clay edge sites) for outer-sphere surface-complex formation. The most abundant minerals found in Yucca Mountain tuff (Bish et al. 1983; Daniels et al. 1982) with a high cation-exchange capacity are listed in Table 20.

In addition to the minerals listed in that table, feldspars may be important cation exchangers in the devitrified tuffs. Cation-exchange capacity for a feldspar is not an intrinsic property because only the external surfaces are available for exchange. Thus, the number of sites depends on the crystal size and morphology.

State of knowledge of cation exchange with respect to Yucca Mountain

As early as 1983 (Daniels et al. 1982), it was shown that the sorption distribution coefficient, K_d , for the adsorption of cesium onto Yucca Mountain tuff could be predicted to within a factor of three using literature data for the cation exchange on the minerals in Table 20 with the addition of analcime. These predictions only considered competition with sodium. This simplification was made because there were no data for the cation exchange of the other alkali metals and alkaline earths present in J-13 well water. Some of the observed scatter could possibly be reduced with these additional data. Unfortunately, over the years since then, the situation has not changed. Thus, there is no predic-

tive model based on mineralogy for cation exchange for radionuclides other than cesium.

We determined the relative contribution of cation exchange to the adsorption of neptunyl onto the zeolitic tuff sample G4-1506 from a sodium-bicarbonate solution. The experiment was based partly on the method of Baeyens and Bradbury. Crushed tuff G4-1506 was equilibrated with 1 M sodium perchlorate to remove alkali metals and alkaline earths by mass action. Solutions containing 0.0022 M sodium bicarbonate (as a pH buffer) were prepared with sodium perchlorate added to provide sodium concentrations that varied from 0.0022 M to 0.22 M. Distribution coefficients for neptunium were determined using the standard procedure (Fig. 91).

The surface complexation of neptunyl has been shown to be inner sphere and noncharging. Therefore, the surface complexation of neptunium is expected to be largely independent of sodium-ion concentration. The results show a linear decrease in K_d with sodium concentration at low sodium concentrations that is consistent with cation exchange (see Eqn. 21). At high sodium concentrations, the K_d asymptotically approaches 2.5 ml/g, consistent with surface complexation. The ion-exchange component is larger than the surface-complexation component, which corresponds to a K_d of about 10 in 0.0022 M sodium bicarbonate. The relatively low K_d for neptunyl in a zeolitic tuff is likely due to the large ion size and high

Table 20. Minerals in Yucca Mountain Tuff with High Cation-exchange Capacities

Mineral	Maximum abundance	Capacity (meq/g)
Clinoptilolite	90 %	2.3
Mordenite	60 %	2.3
Montmorillonite	40 %	0.8–1.5
Illite	20 %	0.13–0.42

hydration number. The K_d in pure sodium bicarbonate solution is larger than that observed in J-13 water; this effect is due to competition with the additional cations in J-13 water of calcium, magnesium, and potassium. A model that describes these data and predicts neptunium sorption in the zeolitic tuff of Calico Hills will be described in the next section.

Surface Complexation

Description of surface-complexation process

The model that we will use to interpret the results of our experiments is the triple-layer surface-complexation model (Davis et al. 1978). The most important difference between this model and conventional chemical equilibria is the effect of surface charge on the activity of ions in the triple layer. This effect is calculated by multiplying the bulk-solution concentration, $[M^+]_{\text{bulk}}$, by a Boltzmann factor

$$[M^+] = [M^+]_{\text{bulk}} e^{-\left(\frac{e\psi_0}{kT}\right)}, \quad (27)$$

where k is the boltzmann constant, T is the absolute temperature, e is electronic charge, and ψ_0 is the potential of the ion in the inner Helmholtz layer.

The charge on the metal-oxide surface is produced by the amphoteric reaction of the metal-oxide surface with acids and bases. The basic charge-producing reactions are with Brönsted acids and bases:



for which the equilibrium constants are:

$$K_{a_1}^{\text{int}} = \frac{[\text{MOH}][\text{H}_3\text{O}^+]}{[\text{MOH}_2^+]} e^{-\left(\frac{e\psi_0}{kT}\right)} \quad \text{and} \quad (30)$$

$$K_{a_2}^{\text{int}} = \frac{[\text{MO}^-][\text{H}_3\text{O}^+]}{[\text{MOH}]} e^{-\left(\frac{e\psi_0}{kT}\right)}. \quad (31)$$

Cations and anions can interact with the electric field near the metal-oxide surface by forming outer-sphere complexes. Ions can also be repelled from the aqueous phase near the metal-oxide surface, as illustrated by Eqn. 16, which can lead to

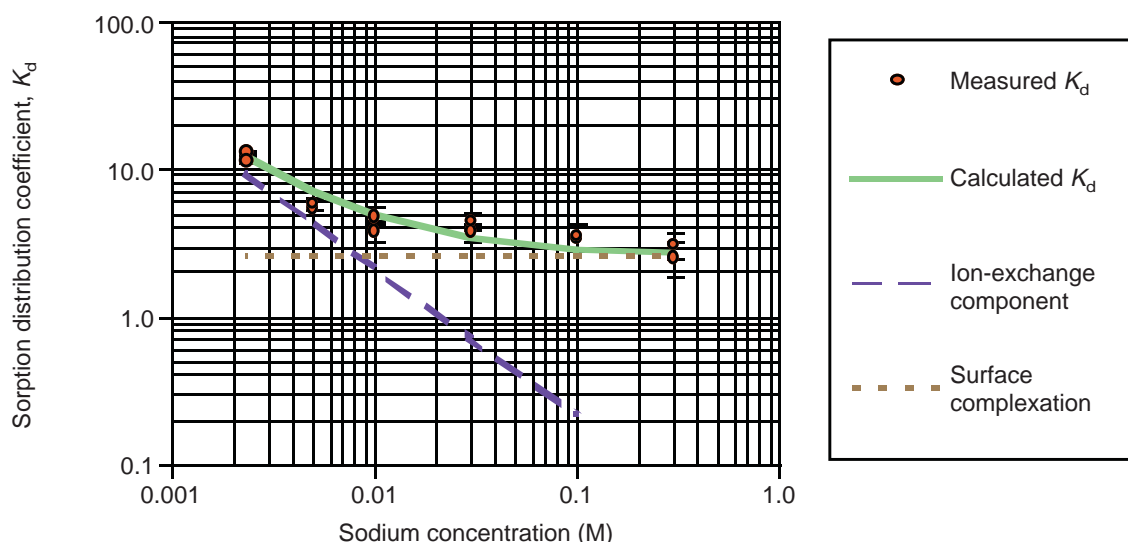


Figure 91. Modeling of Neptunium Sorption. The plot shows data points for the sorption distribution coefficient of neptunium on the zeolitic tuff sample G4-1506 at a pH of 8.4 as a function of sodium ion concentration. Surface complexation should not vary with sodium concentration, so the horizontal dashed asymptote at high concentrations is a measure of surface complexation, and the dashed linear slope at low concentrations is a measure of the ion-exchange component of the sorption.

what appears to be a negative sorption distribution coefficient. This phenomenon is a result of the increase in tracer concentration in the bulk solution due to repulsion of ions from the solution within the double layer. This effect is always small, $K_d > -1$ ml/g. The strict definition of K_d does not allow for negative values because that would imply a negative concentration (which is meaningless). The negative K_d arises because, experimentally, it is impossible to separate the solid phase without including the thin layer of water close to its surface.

Negative K_d values can be used in the same way as positive K_d values and lead to the correct prediction of more rapid migration of excluded tracer with respect to tritiated water, that is, retardation factors less than 1. This phenomenon has been used by van den Hul and Lykelma (1968) to measure the specific surface area of suspended materials. Outer-sphere surface complexation can account for this phenomenon and is represented by the following equations:



where An^- is the anion, Cat^+ is the cation. The equilibrium constants corresponding to these equations are

$$K_{\text{an}}^{\text{int}} = \frac{[\text{MOH}_2^+ \text{An}^-]}{[\text{MOH}_2^+][\text{An}^-]} e^{-\left(\frac{e\psi_\beta}{kT}\right)} \quad \text{and} \quad (34)$$

$$K_{\text{cat}}^{\text{int}} = \frac{[\text{MO}^- \text{Cat}^+]}{[\text{MO}^-][\text{Cat}^+]} e^{-\left(\frac{e\psi_\beta}{kT}\right)} \quad . \quad (35)$$

where ψ_β is the potential of the ion in the outer Helmholtz layer. The ions adsorbed in the outer layer can be exchanged for other ions. The ion-exchange process would be expected to have selectivity differences due to factors such as ion size.

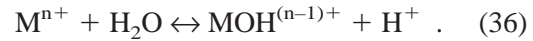
Factors affecting surface complexation

Surface-complexation models are equilibrium models and, therefore, account for speciation reactions explicitly. It is inherently difficult to characterize whole rock, however. This difficulty arises

from the very surface nature of the reactions described. The number of available sites depends on the crystal size and morphology. The identity of available sites depends on the availability of mineral surfaces to the pore water and can be changed by weathering. Given these inherent difficulties, we will attempt to develop a simplified model of surface complexation, including cation exchange.

HSAB (hard-soft acid-base) theory

The surface-complexation coefficients for monodentate surface complexes have been shown to be proportional to the first hydrolysis constant of the aqueous metal ion. This relationship is the natural consequence of the Lewis acid-base theory. The Lewis definition of an acid is an electron-pair acceptor and of a base, an electron donor. The hydrolysis of metal ions in aqueous solution proceeds by reacting with a water molecule displacing a hydrogen ion (an Arrhenius acid) yielding a monohydroxide:



This reaction is analogous to the formation of a monodentate surface complex on a metal oxide, for example, alumina:



The principal difference between these reactions is that the hydroxide ion is the Lewis base in the aqueous hydrolysis reaction (Eqn. 36) and the surface oxygen is the Lewis base in the surface-complexation reaction (Eqn. 37). The strength of the Lewis acid M^{n+} in both reactions is related to the first hydrolysis constant, K_h . The basicity of the surface oxygen is related to the second acid-dissociation constant, K_{a_2} , of the metal oxide. This relationship can be tested by comparing the sum of the logarithms of the surface-complexation constant and the second acid-dissociation constant against the logarithm of the first hydrolysis constant of the metal ion. The $\log K_a$ values for the first and second acid-dissociation constants of metal oxides expected to be found in Yucca Mountain tuff are listed in Table 21. The comparison of literature values (Dzombak and Morel 1990; Kinniburgh et

al. 1976; Huang and Stumm 1973; Schindler 1985) for surface complexation ($\log K_s + \log K_{a_2}$), of metal ions on alumina, silica, and iron oxide are shown in Fig. 92.

The results of this comparison demonstrate that the surface-complexation constant can be estimated to within an order of magnitude, for most metals, given the first hydrolysis constant. A similar comparison for bidentate attachment has yet to be developed, primarily because of the lack of reliable data for bidentate surface complexes.

Description of surface-complexation sites in Yucca Mountain tuff

Although surface complexation has just begun to be studied on Yucca Mountain tuff, there are a number of mineral surfaces having known surface-complexation sites. These are hematite and related iron oxides, silica, and the edge sites of clays. The clay edge sites have been studied and found to be most similar to octahedral alumina (Wieland 1988;

Table 21. Intrinsic Constants for Metal Oxides

Metal oxide	$\log K_{a_1}$	$\log K_{a_2}$	Point of zero charge
SiO ₂	-0.5	-8.2	4.3
Al ₂ O ₃	-7.8	-11.3	9.3
FeOOH	-7.6	-11.4	8.5

Stumm 1992). Although there is no supporting data to determine the relative abundance of these sites, the HSAB approach described above allows one to predict the surface-complexation mechanisms in terms both of stoichiometry and of equilibrium constants.

Modeling of Yucca Mountain tuff

A surface-complexation model for neptunium adsorption onto the zeolitic tuff sample G4-1506 was developed to fit the sodium-concentration

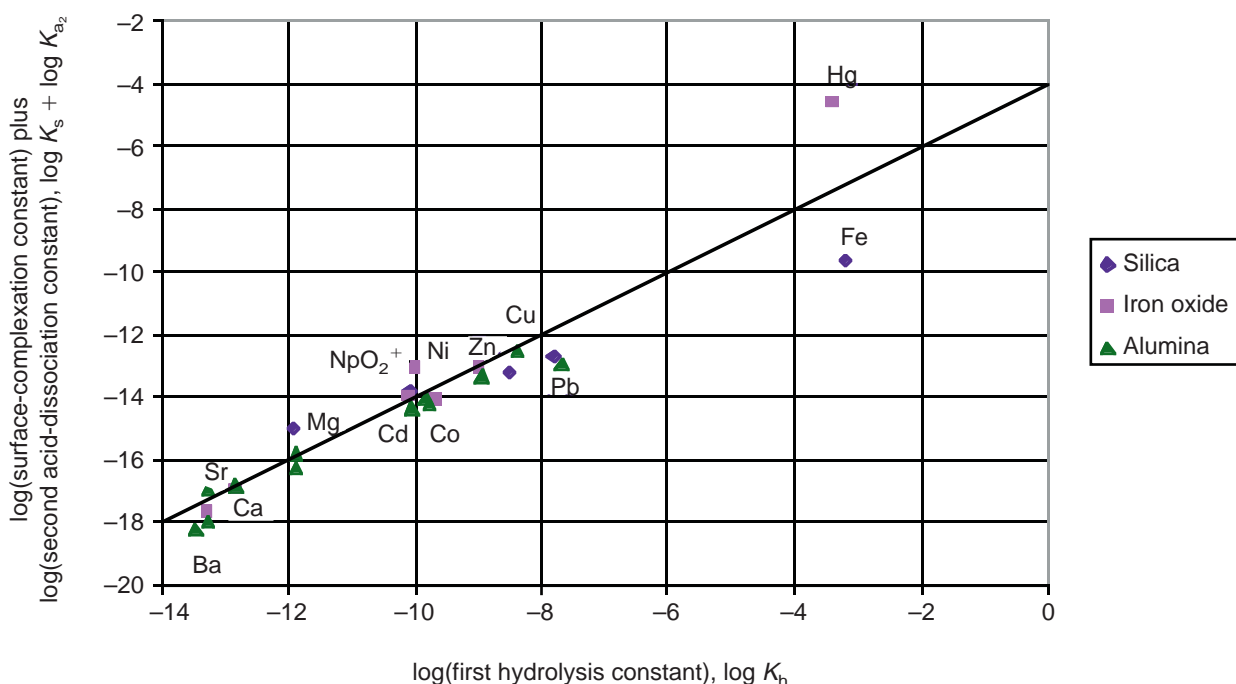


Figure 92. Surface Complexation versus Hydrolysis. This plot compares surface complexation ($\log K_s + \log K_{a_2}$) for monodentate attachment of metal ions with hydrolysis ($\log K_h$) based on the HSAB (hard-soft acid-base) theory.

dependence. The model considered a simple ion-exchange mechanism:



and the formation of an inner-sphere surface complex with octahedral alumina (edge sites) or hematite:



The number of cation-exchange sites available to neptunium (Table 22) was based on the apparent saturation of sites observed in a neptunium adsorption isotherm measured for tuff sample G4-1608 in a carbon-dioxide atmosphere (Thomas 1987). The neptunium-exchange capacity is four orders of magnitude smaller than the cation-exchange capacity of clinoptilolite (Table 20). This difference can be explained by the large size of the hydrated nep-

tunyl ion. If no sorption occurs in the intracrystalline channels of the clinoptilolite, the maximum exchange capacity will be on the order of a μmole per gram, assuming a 3- μm crystal diameter. The selectivity for neptunium was used as an adjustable parameter, and the model was fit to the results of the sodium-ion dependence of neptunium adsorption onto tuff sample G4-1506.

The inner-sphere surface complexation of neptunium was modeled assuming that surface complexation occurs primarily on clay edge sites or iron-oxide surfaces. The constant for inner-surface complexation of neptunium onto iron oxide was used because the analogous constant for alumina is expected to be nearly equal on the basis of the HSAB theory shown above. Thus, the second adjustable parameter was the edge-site density.

Table 22. Equations and Parameters Used to Model Neptunium Adsorption onto Zeolitic Tuff

Type of reaction	Equilibrium reactions	log K
Aqueous reactions:	$\text{NpO}_2^+ + \text{H}_2\text{O} \leftrightarrow \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$	-10.8
	$\text{NpO}_2^+ + 2\text{H}_2\text{O} \leftrightarrow \text{NpO}_2(\text{OH})_2^- + 2\text{H}^+$	-23.5
	$\text{NpO}_2^+ + \text{CO}_3^{2-} \leftrightarrow \text{NpO}_2\text{CO}_3^-$	4.13
	$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	-10.25
	$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$	-7.8
Metal-oxide surface protolysis:	$\text{MOH} + \text{H}^+ \leftrightarrow \text{MOH}_2^+$	7.6
	$\text{MOH}_2^+ + \text{ClO}_4^- \leftrightarrow \text{MOH}_2^+\text{ClO}_4^-$	2.0
	$\text{MOH} \leftrightarrow \text{MO}^- + \text{H}^+$	-11.4
	$\text{MO}^- + \text{Na}^+ \leftrightarrow \text{MO}^-\text{Na}^+$	1.2
Neptunyl adsorption reactions:	$t\text{-Al}^-\text{Na}^+ + \text{NpO}_2^+ \leftrightarrow t\text{-Al}^-\text{NpO}_2^+ + \text{Na}^+$	2.1
	$\text{MOH} + \text{NpO}_2^+ \leftrightarrow \text{MONpO}_2 + \text{H}^+$	-2.2
Extension to groundwater:	$2t\text{-Al}^-\text{Na}^+ + \text{Ca}^{2+} \leftrightarrow t\text{-Al}_2^{2-}\text{Ca}^{2+} + 2\text{Na}^+$	5.0
	$\text{MOH} + \text{Ca}^{2+} \leftrightarrow \text{MOCa}^+ + \text{H}^+$	-5.85
	$\text{MOCa}^+ + \text{Cl}^- \leftrightarrow \text{MOCa}^+\text{Cl}^-$	2.0

Parameters			
Type of site	Site density (eq/kg)	Layer	Capacitance (F/m ²)
Tetrahedral (t) aluminum	2×10^{-4}	Inner Helmholtz	1.1
Octahedral aluminum (edge)	3×10^{-6}	Outer Helmholtz	0.2

To extend this model to the empirical measurements done under the project's geochemistry program, additional assumptions were made. The competition of cations in groundwater for cation-exchange sites was based on the selectivities derived from measurements on the mineral tobermorite (Tsuji and Komarneni 1993). This approach was the result of the argument explaining the reduced cation-exchange capacity for neptunium. If exchange occurs only on the exterior of the zeolite crystal, then steric effects must be avoided. Tobermorite offers an open structure that could be expected to have less steric effects than a zeolite. Furthermore, that work showed little difference between magnesium and calcium so that both magnesium and calcium were treated as one competitor. There were no data for potassium, so competition with potassium was not considered.

The surface-complexation constant for calcium was taken from the HSAB theory. Thus, there were no additional adjustable constants. The concentrations used for J-13 and UE-25 p#1 well water are shown in Table 23. The calculations were made using the FITEQL code in the forward mode only, that is, no fitting. The results of the modeling are shown in Figs. 93 and 94. The agreement between the model calculations and the measured results were in general excellent. The correct pH dependence was predicted for the dry-sieved samples; the wet-sieved samples agreed better with a calculation that had no surface-complexation sites. The implications of these results are not yet fully understood. Two possibilities are that either the clay particles are washed out, reducing the available edge sites, or that a trace component of J-13 water is forming a strong surface complex that competes with neptunium. The model also predicted the observed reduction in the sorption distribution coefficient, K_d , due to the components of UE-25 p#1 water. In this water, the higher carbonate concentration eliminates the contribution of surface complexation observed in J-13 water at pH values above 7.

A model was also developed for pH dependence of

Table 23. Groundwater Compositions Used for Neptunium Sorption Modeling

Constituent	Concentration (mg/l)		
	J-13 water	UZ water	UE-25 p#1 water
Sodium	45	26–70	171
Potassium	5.3	5–16	13.4
Magnesium	1.8	5–21	31.9
Calcium	11.5	27–127	87.8
Silicon	30	72–100	30
Fluoride	2.1	–	3.5
Chloride	6.4	34–106	37
Sulfate	18.1	39–174	129
Bicarbonate	143	–	698
pH	6.9	6.5–7.5	6.7

uranium adsorption onto crushed devitrified tuff. This treatment was similar to that used to model neptunium adsorption except that 1) the cation-exchange capacity for uranium was not known (that is, there was no adsorption isotherm) and 2) a cation exchange with the monohydroxy-uranyl complex was included. The parameters used are listed in Table 24. The number of sites used to model these data was much greater than for the zeolitic tuff. The possible reason for this is the exposure of fresh surfaces of feldspar and quartz combined with the lack of exposure to a complex groundwater.

The results of this exercise are shown in Fig. 95 and are in excellent agreement with the results of Leckie and his students (Davis et al. 1978). The equilibrium concentration of uranium at pH values of 9 and above are above the solubility limit for uranium hydroxide. The effect of precipitation was evident in the experimental data. The solubility product was not included in this model.

State of knowledge of surface complexation with respect to Yucca Mountain

Surface-complexation reactions with Yucca Moun-

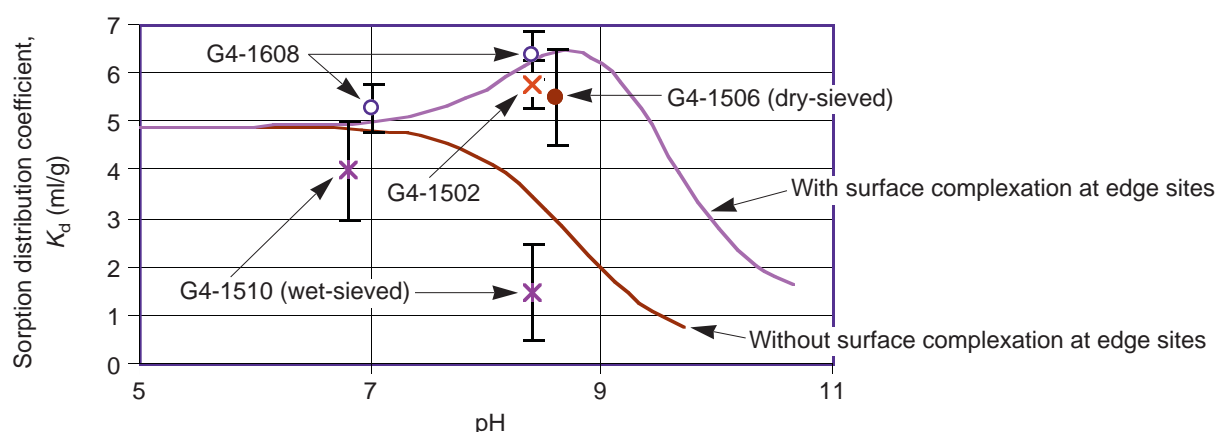


Figure 93. Neptunium Sorption in J-13 Water. This plot compares sorption data (points) with the predictions of the FITEQL code for the pH dependence of neptunium sorption on zeolitic tuff from J-13 water with and without surface complexation at edge sites (curves). The sorption data for samples G4-1608 and G4-1502 are from Thomas (1987).

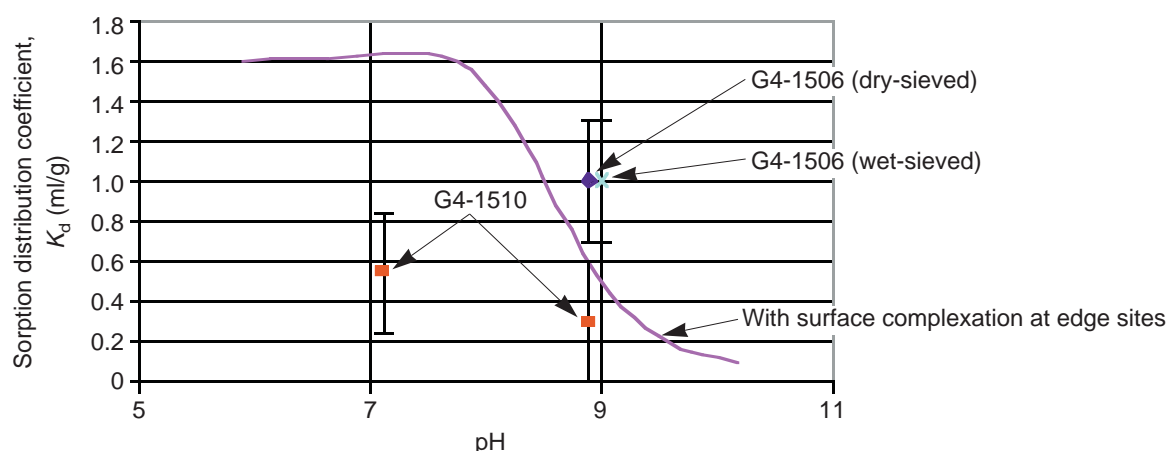


Figure 94. Neptunium Sorption in UE-25 p#1 Water. This plot compares sorption data (points) with the predictions of the FITEQL code for the pH dependence of neptunium sorption on zeolitic tuff from UE-25 p#1 water with surface complexation at edge sites (curve).

tain tuff have just begun to be studied. The pH dependence of actinide adsorption can be readily explained with a combined surface-complexation and ion-exchange model. The effect of changing groundwater composition on neptunium adsorption has also been successfully modeled using a surface-complexation model. There are significant gaps in the knowledge base, however. From a fundamental standpoint, an HSAB model for bidentate inner-sphere complexes needs to be developed. The consequences of a bidentate attachment mech-

anism, as was included in the uranium adsorption model, is an increased sensitivity to competition with metal ions favoring monodentate attachment (for example, calcium). From an experimental standpoint, the effects of wet-sieving needs to be better understood. If wet-sieving removes all of the clay minerals, the resulting distribution coefficients may be too low (overly conservative). On the other hand, if a trace component of groundwater is responsible for the decrease in surface complexation, it must be identified and measured in

Table 24. Additional Equations and Parameters Used to Model Uranium Adsorption onto Devitrified Tuff

Type of reaction	Equilibrium reactions	log K
Aqueous reactions:	$\text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.8
	$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_2 + 2\text{H}^+$	-12.5
	$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.62
	$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.63
Uranyl adsorption reactions:	$2t\text{-Al}^-\text{Na}^+ + \text{UO}_2^{2+} \leftrightarrow (t\text{-Al}^-)_2\text{UO}_2^{2+} + 2\text{Na}^+$	1.8
	$t\text{-Al}^-\text{Na}^+ + \text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow t\text{-Al}^-\text{UO}_2\text{OH}^+ + \text{Na}^+ + \text{H}^+$	-1.5
	$\text{MOH} + \text{UO}_2^{2+} \leftrightarrow \text{MOUO}_2^+ + \text{H}^+$	0.60
	$\text{MOH} + \text{UO}_2^{2+} + \text{Cl}^- \leftrightarrow \text{MOUO}_2^+\text{Cl}^- + \text{H}^+$	2.8
	$2\text{MOH} + \text{UO}_2^{2+} \leftrightarrow (\text{MO})_2\text{UO}_2 + 2\text{H}^+$	-2.8
Parameters:	Type of site	Site density (eq/kg)
	Tetrahedral (t) aluminum	2×10^{-2}
	Octahedral aluminum (edge)	2×10^{-3}

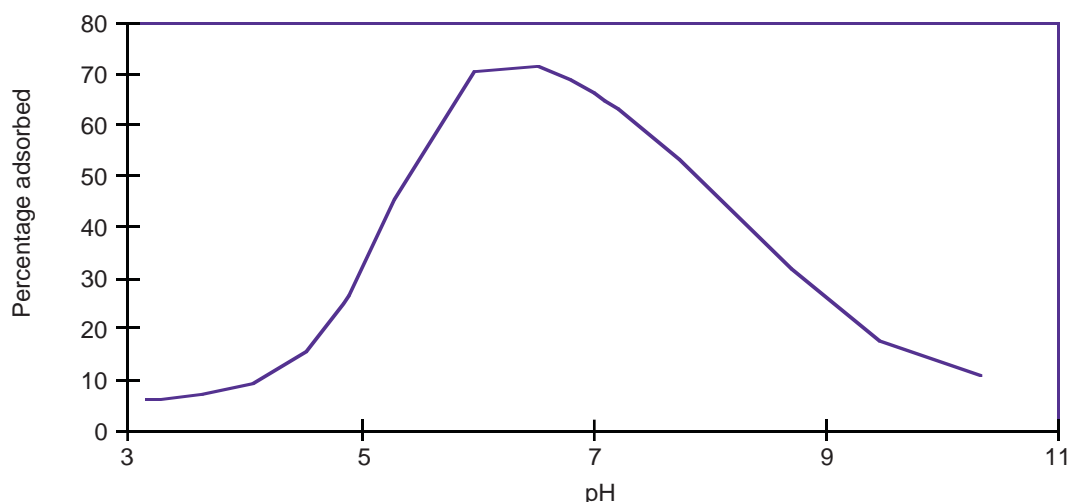


Figure 95. Uranium Adsorption. The curve above shows the predictions of the FITEQL code for the adsorption of uranium onto crushed devitrified tuff from an 0.1 M sodium-chloride solution in a controlled atmosphere with an initial uranium concentration of 1×10^{-6} M.

groundwaters and in pore waters.

The modeling of actinide sorption shows that high carbonate concentrations will severely reduce the ability to form surface complexes on tuff. The ion exchange of actinides appears to dominate under

normal conditions over surface complexation.

Furthermore, divalent cations are found to be strong competitors for cation-exchange sites found in Yucca Mountain tuff.